PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-295614
(43)Date of publication of application : 21.10.1994

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(51)Int.CI.
H01B 1/16
C04B 41/88
C09D 5/24
C09D 7/12
H01C 1/14
// H01G 1/14

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(21)Application number : 05-080517
(22)Date of filing : 07.04.1993
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(54) CONDUCTIVE PASTE FOR BAKING

(57)Abstract:

PURPOSE: To provide viscous copper alloy conductive paste which is stable enough even in the printing with a fine line and has long-term preservability, not to speak of having resistance to oxidation.

CONSTITUTION: Paste for baking is expressed by general formula AgxCu1-x (but, $0.001 \leq X \leq 0.4$, atomic rate), and the concentration of silver on the surface is higher than average concentration of silver, and besides, it has a region where the concentration of silver increases toward surface. Furthermore, it comprises 100 pts.wt. of copper alloy powder containing 0.1-1000ppm of titanium components, 0.1-30 pts.wt. of glass frits, and organic vehicles. As a result, as compared with conventional copper paste, it is not only excellent in resistance to oxidation at baking but also excellent in resistance to oxidation in preservation of paste, therefore it gives stable viscosity property even at printing of a fine line circuit and at long-term preservation.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]
[Claim 1] The paste for baking characterized by to contain the glass frit 0.1 - 30 weight sections, and an organic vehicle to the electric conduction powder 100 weight section which is expressed with a general formula Agx Cu 1-x (4 however, 0.001<=x<=0. x atomic ratio), and the silver concentration on the front face of a particle is higher than average silver concentration, and has the field which silver concentration increases toward a front face near the front face, and has 0.1-1000 ppm of titanium components on a particle front face.
[Claim 2] The paste for **** characterized by a glass frit according to claim 1 containing 0.1-1000 ppm of titanium components.
[Claim 3] The paste for baking which comes to carry out 0.1-15 weight section content of one or more sorts of oxide powder further chosen as the baking paste according to claim 1 or 2 from copper I oxide, a cupric oxide, the bisumuth oxide, oxidation ******, lead oxide, cadmium oxide, a zinc oxide, oxidation silicon, a calcium oxide, oxidation tin, an aluminum oxide, and barium-oxide powder to the electric conduction powder 100 weight section.
[Claim 4] The paste for baking whose oxide powder according to claim 3 comes to contain 0.1-1000 ppm of titanium components.
[Claim 5] The paste for baking which it comes to contain during a paste in the paste for baking according to claim 1 to 4 0.1-1000 ppm to the copper alloy powder 100 weight section.
[Claim 6] The electric conduction circuit using the paste for baking according to claim 1 to 5.
[Claim 7] The stacked type ceramic condenser external electrode using the paste for baking according to claim 1 to 5.
[Claim 8] The low-temperature baking multilayered circuit board outer conductor using the paste for baking according to claim 1 to 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention is applicable to a hybrid IC electric conduction circuit, a stacked type ceramic condenser external electrode, a low-temperature baking multilayered circuit board outer conductor, a low-temperature baking multilayered circuit board inner conductor, a stacked type ceramic condenser internal electrode, an LC filter outer conductor, a resistor terminal electrode, etc. about the conductive paste for baking.
[0002]
[Description of the Prior Art] Before, the thing using powder, such as a silver, gold, platinum, silver-palladium, copper, and copper-silver alloy, as conductive paste for baking is well-known. It was printed or applied on the ceramic substrate, radical sintering was calcinated and carried out at about 600-900 degrees C, and these well-known pastes have been used as a conductor. In the thing using exotic powdered metals, such as silver, gold, platinum, and silver-palladium, it is calcinated, sintered and used in air and, in the case of copper and copper alloy powder, sintering has been performed in the inert atmosphere which used nitrogen etc. as the principal component. It is a glass frit and viscosity control in order to give the adhesive strength with a substrate other than electric conduction powder, although prepared using said electric conduction powder as a conductive paste for baking. The organic vehicle which used well-known ethyl cellulose, acrylic resin, butyral resin, etc. with the solvent has been used.
[0003] Using these conductive pastes, a circuit or when carrying out electrode formation, printing by the screen and dip spreading are used for the ceramic substrate or the chip. In screen-stencil etc., while fine line-ization of a circuit progresses, printing around 100 micrometers is needed for circuit width of face. Therefore, in mass production etc., the stability of paste viscosity has been needed more. When paste viscosity was too high, the blur arose in the printed circuit, an open circuit tended to start it, the printed circuit became bored by it with hypoviscosity past **, and the stability under viscosity control and preservation of viscosity was required for it in short-circuiting with next Rhine.
[0004]
[Problem(s) to be Solved by the Invention] everything but a cost rise in the paste using exotic powdered metals, such as gold shown above, platinum, palladium, and silver, -- formation -- a conductor -- there are migration between circuits and a problem of a solder foods crack, and use is difficult for a RF circuit, a high density circuit, and high density assembly. Although the combination of silver-palladium, silver-platinum, etc. is well-known, since palladium with high resistance and platinum are used, conductivity is bad and use Rhine width of face is limited.
[0005] As the paste for baking using copper powder is shown above, although some technical problems occur and various attempts have so far been reported, the trouble that the oxidation resistance of copper powder is bad is not still solved in essence. Copper oxidation resistance has brought about bad various evils. That is, even if it was baking among nitrogen, the soldering nature of the sintering film was bad and the shelf life of the sintering film itself did not have it, either. Moreover, oxidation on the front face of copper powder distributed also in the paste progresses gradually, and it has the fault from which coherent [in an organic vehicle] and concordance also change by forming oxide in a copper powder front face during the usual paste retention period, and paste viscosity changes. Therefore, for the application which needs the stability of viscosity like 100-micrometer Rhine printing, the solvent had to be specially added, readjusted and used at the time of an activity.
[0006] Therefore, although the attempt which adds a copper acid-ized inhibitor to a paste also occurs (for example, JP,4-277406,A), do not take remarkable days for viscosity to become stability by adding, or viscosity does not become instability, or since it is copper powder too, it has not resulted in essential antioxidizing.
[0007]
[Means for Solving the Problem] This invention is expressed with a general formula Agx Cu 1-x (4 however,

0.001<=x<=0. x Hara ratio). And the electric conduction powder 100 weight section which the silver concentration on the front face of a particle is higher than average silver concentration, and has the field which the degree of silver increases toward a front face near the front face, and has 0.1-1000 ppm of titanium components on a particle front face is received. The baking paste electric conduction powder 100 weight section of this presentation is received in more detail about the paste for baking characterized by containing the glass frit 0.1 - 30 weight sections, and an organic vehicle. Furthermore, copper I oxide, a cupric oxide, the bisumuth oxide, oxidation ******, lead oxide, It is related with the conductive paste for baking which comes to carry out 0.1-15 weight section addition of the one or more sorts chosen from oxidization KAMIUMU, a zinc oxide, oxidization silicon, a calcium oxide, oxidization tin, and aluminum oxide-ized barium powder. As for the copper alloy powder used by this invention, it is desirable to be produced by the approach already indicated by JP,02-282401,A for which these people apply. Especially, it is good to use the inert gas atomizing method. It blows off and the high-speed flow which generated gas, such as nitrogen, an argon, helium, and hydrogen, or the mixed gas chosen from these by adiabatic expansion to the copper of this presentation and silver melt as an inert gas atomizing method is impalpable-powder-ized. 5kg/cm2 or more is desirable and the pressure before adiabatic expansion is 15kg/cm2 further. The above is desirable. In case the melt of this presentation is atomized, it is desirable that it is the temperature of 1200 degrees C or more. As for the gas / melt mass-velocity ratio when atomizing, two or more are desirable. Although the copper alloy powder used by this invention is silver contents 0.001-0.4, oxidation resistance is inadequate in it being less than 0.001, and oxidation of the front face at the time of paste preservation progresses. Therefore, the viscosity of a paste rises. In exceeding 0.4, the problem of silver migration arises. Preferably, it is 0.01-0.22. Moreover, although the surface silver concentration of the copper alloy powder used by this invention is higher than average silver concentration, 2.1 or more-time 80 or less times of average silver concentration are desirable, and 3 or more-time 30 or less times are still more desirable. Moreover, although it has the field which silver concentration increases toward a front face near the front face, copper oxidation resistance can be improved because surface silver concentration is high, and silver migration can be prevented by giving a concentration gradient. In silver plating copper powder, in order that the prevention effectiveness of surface silver cannot improve and may raise oxidation resistance in the mechanical alloying of silver and copper, a lot of silver is not needed and desirable. It is the description that the copper alloy powder used by this invention contains 0.1-1000 ppm of titanium components. The titanium component used by this invention shows the total quantity of the titanium component which exists as a titanium metal and a titanium compound (an organic titanium compound, inorganic titanium compound). Especially, an organic titanium compound is desirable.

[0008] as an organic titanium compound -- R1-Ti-(R2) 3 (the inside R1 of a formula -- carbon numbers 1-4 -- desirable -- the ARUKOKI radical of carbon numbers 1-3, and R2 -- carbon numbers 2-20 -- the carboxylate of carbon numbers 2-18 is mentioned preferably.) For example, isopropyl TORIISO stearyl titanate, isopropanal PIRUTORI octanoyl titanate, Isopropyl tris (dioctylpyrophosphate) titanate, Isopropanal PIRUTORI (N-aminoethyl aminoethyl) titanate, Tetra-octyl screw (JITORIDE sill phosphate) titanate, tetrapod (2 and 2-diaryl oxymethyl 1-butyl) screw (JITORIDESHIRU) phosphate titanate, Screw (dioctylpyrophosphate) oxy-acetate titanate, Screw (dioctyl PAIRO phosphate) ethylene titanate, isopropyl JIMETA acrylic isostearoyl titanate, They are isopropyl ISOSUTEAROIRUJI acrylic titanate, isopropanal PIRUTORI (dioctyl phosphate) titanate, isopropyl TORIKUMIRU phenyl titanate, TETORO isopropyl screw (dioctyl phosphate) titanate, etc.

[0009] It is desirable to exist in a copper alloy powder front face as a titanium component. For example, concordance with an organic vehicle and dispersibility become good by containing a copper alloy particle front face about an organic titanium compound, and the hat of the viscosity rise by the condensation under preservation etc. can be carried out. Moreover, it is that there is no problem of a rise of the viscosity by deteriorating to a copper acid ghost gradually like a copper grain child front face in silver existing in a copper alloy front face at high concentration. That is, since it exists mainly in the front face of a silver component also when an organic titanium compound is made to exist in a particle front face, since silver concentration is high on a particle front face, a stable paste without a viscosity rise is obtained.

[0010] Although it comes to contain 0.1-1000 ppm in the appearance shown above as an amount of titanium components, in the case of less than 0.1 ppm, the stability of viscosity is bad, and flocking settling of a particle happens to it. In exceeding 1000 ppm, there are too many surface titanium components and they check sintering of a copper alloy particle. It is 0.5-300 ppm and is 1-100 ppm more preferably.

[0011] The titanium quantitative formula of a copper alloy particle is the value which dissolved copper alloy powder in concentrated nitric acid completely, and was measured by ICP (product made from the SEIKO electronic industry :). In this case, the copper alloy particle of this presentation means containing the amount of titanium components of the amount shown above also in a paste on the particle front face. Measurement of the amount of titanium components is the copper alloy particle after separating a copper alloy particle with solid content by centrifugal separation in the case of the copper alloy powder under paste Filtration and 50 degrees C 3 hours After processing with a vacuum dryer under reduced pressure of 100 or less mHgs, it measures by said ICP.

[0012] The paste for baking of this invention can use what has a well-known glass frit, although glass frit 0.1-30 weight section content is carried out to the copper alloy powder 100 weight section. For example, PbO-B2 O3-ZnO and PbO-B2 O3-SiO2, PbO-B2 O3-SiO2-ZnO, PbO-SiO2-ZnO, PbO-SiO2-CaO, PbO-SiO2-BaO, PbO-SiO2-B-2 O3-CaO, PbO-B2 O3-BaO, PbO-B2 O3-CaO, PbO-B2 O3-SiO2-ZnO, etc. are mentioned. Although it does not limit to especially these glass frits, that whose softening temperature is 300-500 degrees C is desirable especially. As magnitude of a glass frit, that in which an about 0.1-10-micrometer thing is contained 70% or more is desirable as particle diameter. It is not specified especially about a configuration. When the addition of a glass frit does not show bond strength sufficient by less than 0.1, but exceeds 30 weight sections, and a glass component is sintering, it comes up to a front face and poor soldering is caused. It is 0.5 - 15 weight section, and is 1 - 10 weight section more preferably.

[0013] Moreover, as for the glass frit of this invention, it is desirable to contain a titanium component like copper alloy powder. As a titanium component, the same titanium compound as copper alloy powder can be used. Also in this case, it is desirable to contain 0.1-1000 ppm so that flocking settling of a under [the paste of a glass frit] may not happen. When flocking settling tends to happen in the case of less than 0.1 ppm and it exceeds 1000 ppm in it, the softening temperature of a glass frit is changed and the conductor of sufficient reinforcement is not obtained. Preferably, it is 0.2-500 ppm. It is the value measured by ICP like copper alloy powder.

[0014] Although the paste for baking of this invention contains the organic vehicle, it gives moderate viscosity, thixotropy nature, and printing nature to a paste as an organic vehicle. The organic binder and solvent which carry out vaporization, decomposition, or depolymerization are fully shown at the time of baking. For example, well-known things, such as ethyl cellulose, hydroxyethyl cellulose, methyl cellulose, butyral resin, acrylic resin, and phenol resin, can be used. Preferably, they are ethyl cellulose and acrylic resin. As acrylic resin, the polyvinyl butyral resin of for example, Pori methacrylic acid butyl ester, Pori methacrylic acid isobutyl ester, and lower alcohol is desirable. As a solvent, TERUPE Norian, methyl carbitol, butyl carbitol, Ethyl carbitol, ethylcellosolve, butyl cellosolve, methyl carbitol acetate, Butyl carbitol acetate, ethyl carbitol acetate, butyl-cellosolve acetate, Ethylcellosolve acetate, butyl acetate, ethyl acetate, 2 and 2, 4-trimethyl 1, 3 pentanediol monochrome iso butyrate, 2, 2, and 4-trimethyl -- although 1, 3, pentanediol JIISO butyrate, dibutyl phthalate, alpha, beta TERUPE Norian, octyl alcohol, etc. are mentioned, it is good at an especially well-known solvent. As amount of the organic vehicle used, the 0.1 - 200 weight section is desirable to the electric conduction powder 100 weight section, and the 0.1 - 100 weight section is still more desirable.

[0015] Although the paste for baking of this invention comes to contain a titanium component to copper alloy powder, the titanium component may exist in an organic vehicle. however -- the case where it exists so much -- viscosity -- very much -- being stabilized -- ****** -- it is not desirable. Preferably, 0.1-1000 ppm may exist to the copper alloy powder 100 weight section during a paste.

[0016] In order to improve the adhesive strength of the sintered compact at the time of baking, and a substrate to the paste for baking of this invention, powder, such as copper I oxide, a cupric oxide, the bisumuth oxide, the barium oxide, lead oxide, a zinc oxide, oxidation ******, silicon oxide, tungstic oxide, an iron oxide, manganese oxide, cadmium oxide, tungstic oxide, chrome oxide, oxidation tin, a magnesium oxide, and a tungsten metal, can also be added. In this case, it can add to 0.1 - 15 weight section to the copper alloy powder 100 weight section. The particle diameter of metallic-oxide powder has that desirable whose 70% or more exists in the 0.1-15-micrometer range.

[0017] The thing which comes to contain a titanium component in the case of this metallic-oxide powder as well as copper alloy powder and a glass frit is desirable. 0.1-1000 ppm can be contained as a content. In less than 0.1 ppm, in flocking settling's tending to happen and exceeding 1000 ppm, the effectiveness for the improvement in bond strength worsens. Preferably, it is 0.4-500 ppm. It is the value measured using ICP like copper alloy powder.

[0018] Moreover, an anti-oxidant (for example, triazole compounds, such as a higher fatty acid, a linolenic acid, a palmitic acid, oleic acid, stearin acid, linolic acid and such copper salt, benzotriazol, and tolyl triazole, polymer phosphate), a CHIKISO agent dispersant (silane coupling, aluminum coupling, zirconium coupling agent), etc. can also be added if needed. Moreover, a well-known plasticizer can also be used. In this case, to the copper alloy powder 100 weight section, 0.001-15 weight section addition can be carried out, and it can also use.

[0019] although it prints, or applies and uses when using the paste for baking of this invention, a well-known thing carries out as a ceramic substrate -- a way can be carried out. for example, ceramic substrates, such as an alumina, and ****, an alumina, cordierite, a mullite, a steer light, the inner layer green sheet of the substrate for low-temperature baking which used the glass component as the principal component, and an outer layer -- it can apply as a conductor, and a tantalum condenser, the stacked type ceramic condenser external electrode using a titanate and the external electrode of an LC filter, and can use.

[0020] It is desirable to make it sinter at 500-1000 degrees C as a burning temperature, and, as for an ambient atmosphere, it is desirable to calcinate in the inert atmosphere in nitrogen-gas-atmosphere mind etc. The well-known approach calcinated using a band-conveyor type continuous furnace is sufficient as a firing furnace. At this time, it is desirable from doping oxygen at the temperature of about 200-500 degrees C fully burning an organic vehicle off.
[0021] Since especially the paste for baking of this invention is excellent in oxidation resistance, even if it adds hundreds of ppm oxygen, it does not spoil a property not to mention the ability to calcinate in the ambient atmosphere strictly managed by 10 ppm or less like the well-known copper paste. Although the example of the baking paste of this invention was shown below, each property was measured on condition that the following.
Using the silver of the front face of copper alloy powder, and the copper density measurement XPS (X-ray-photoelectron-spectroscopy analysis apparatus; XSAM [800], product made from KRTOS), electric conduction powder was stuck on the sample base, and it measured by 12kV, 10mA, and 10in argon gas ambient atmosphere-8torr. Etching conditions are 2KeV. Argon gas spatter 10-7torr It carried out for 5 minutes. Measurement made the average of measurement, and a 5 times repeat deed and the first two measurement of etching surface silver concentration and surface copper concentration.
[0022] Silver concentration x=Ag/(Ag+Cu), copper concentration 1-x=Cu/(Ag+Cu)
(Atomic ratio) Average silver and copper concentration dissolved copper alloy powder into concentrated nitric acid, and measured it by ICP.
The value when measuring the viscosity property at the time of paste viscosity change paste production by 10rpm with B mold rotational viscometer was used. At this time, paste viscosity made the set point the range of 150 - 350 Pa-s. Moreover, the case where the viscosity rate of change of one month after was less than 30% was made good.
It dissolved in the concentrated-nitric-acid solution, and the amount copper alloy powder of titanium components, the glass frit, and the titanium component of a metallic oxide were measured by ICP. About what is not dissolved, it is EPMA (Horiba EMAX- 2200) acceleration voltage 5-20kv about said powder. Addition It analyzed by time amount 300 seconds.
[0023] After the titanium component in an organic vehicle carried out solid liquid separation of the paste, it diluted the organic vehicle solution with benzyl alcohol, and measured it by ICP.
5mm angle of conductive trials and 15-micrometer baking film pad in thickness were produced, and conductivity (resistance) was measured by 4 terminal method. 1.5 - 4.5mohm/** was made good.
[0024] Moreover, 120-micrometer Rhine was printed independently and conductivity (resistance) was checked. Also in this case, 1.5 - 4.5mohm/** was made good.
2mm angle pad of soldering sex test was produced, and the wetted area when dipping the baking film into 230 degrees C of Sn/Pb eutectic solder baths for 5 seconds made 90% or more good. Moreover, it is 150 degrees C among air. The wettability after 2-hour neglect was also examined.
The sintering film of migration trial 1mmgap is produced, 0.2ml purity was dropped at gap, the seal of approval of the 50 direct current voltage was carried out between sintering film, and the time amount when exceeding 100microA to inter-electrode made 300 seconds or more good.
A leadframe (0.5mmx1.5mm) is put between the film (15 micrometers in thickness) sintered by 2mm angle pad of adhesive strength tests with a substrate, and it is 230 degrees C. After dipping for 5 seconds during an eutectic solder bath, reinforcement at the time of peeling of the film at the time of ******** was perpendicularly made into bond strength the rate for bending and 50mm/. Moreover, 150 degrees C The reinforcement after 1000-hour neglect was also measured. 1.6kg or more was made good.
[0025]
[Example] Production of copper alloy powder was produced on the conditions shown in Table 1.
[0026]
[Example 1] The powder of the example 1 of powder production was classified with the air-current classifier by 10 micrometers or less. The obtained powder was 5 micrometers in mean particle diameter. It is 3 in 100g of obtained classification a ten to 4 g/cm organic titanium compound (isopropyl TORIISOSUTE aisle titanate). It processed stirring in a toluene solution for 2 hours. Solid liquid separation was carried out by the back fault of it. The titanium component was 13 ppm when the obtained powder was measured by ICP.
[0027] Processing powder was taken out, the glass frit PbO-B2 O3-ZnO(412 degrees C of softening temperatures) 7 weight section, the copper I oxide powder 3 weight section, the ethyl cellulose 0.3 weight section, the butyl carbitol acetate 2 weight section, and the ethylcellosolve 2 weight section were mixed to the powder 100 weight section, and it considered as the paste. Although viscosity was 300 Pa-s, it was stable with 305 Pa-s also after one-month neglect.
[0028] Obtained PEZUTO is printed on an alumina substrate and it is 900 degrees C. It calcinated for 10 minutes in

nitrogen-gas-atmosphere mind. At this time, it doped 30 ppm of oxygen to 500 degrees C. The conductivity of the obtained baking film was good by 2microomega. The migration-proof trial was also as good as 300 seconds. It is high and bond strength is [3kg and] 150 degrees C. There was 2kg or more also after 1000-hour neglect. Solder wettability is also 230 degrees C. Solder **** is good ****** enough also after 2-hour neglect.

[0029]

[Example 2] 5 micrometers or less of the powder obtained in the example 2 of powder production were classified with the air-current classifier. The obtained classification powder is 3 micrometers and is the 100g 10-3 g/cm3 of an organic titanium compound (isopropanal PIRUTORI octanoyl titanate) It stirred in the toluene solution for 2 hours. Then, solid liquid separation was filtered and carried out. The titanium component was 1 ppm when the obtained powder was measured by ICP. Furthermore, receive the powder 100 weight section. The PbO-SiO2-B-2 O3-ZnO (470 degrees C of softening temperatures) glass frit (the amount of titanium components of 3 ppm) processed with the same organic titanium compound as copper alloy powder One weight section, The cupric-oxide powder (amount of titanium components of 3 ppm) 1 weight section processed with the same, same organic titanium compound as copper alloy powder, The bisumuth-oxide 1 weight section, the Al Lil resin 3 weight section, the silicon defoaming agent 0.01 weight section, 2 and 2, 4-trimethyl 1, the 3 pentanediol monochrome iso butyrate 3 weight section, and the alpha-TERUPE Norian 1 weight section were added, and it considered as the paste. The viscosity of a paste is 260 Pa-s and was almost changeless also after one month at 255 Pa-s.

[0030] The obtained paste was screen-stenciled on the glass substrate. Furthermore, it calcinated for 20 minutes in 600-degree-C nitrogen-gas-atmosphere mind. At this time, it doped 100 ppm of oxygen to 550 degrees C. The resistance of the obtained conductor was as good as 2mohm/**. Migration-proof nature was also as good as 310 seconds. It is high and bond strength is [3kg and] 150 degrees C. It was as good as 2.5kg also after 1000 hours. Solder wettability is also 230 degrees C. It was enough also after 2-hour neglect.

[0031] moreover, the interior -- a silver conductor -- the mullite [which has a circuit], and six-layer multilayered circuit board top which used glass as the principal component -- screen-stenciling -- 900 degrees C It calcinated in nitrogen-gas-atmosphere mind (200 ppm dope of oxygen to 500 degrees C). Resistance was as good as 2mohm/**. Moreover, it applied as an outer conductor of value-of-standard capacity (mF) stacked type ceramic condenser of 1micro which has nickel in an internal electrode. 760 degrees C It calcinated in nitrogen-gas-atmosphere mind for 10 minutes. Capacity was as good as **20% of the value of standard.

[0032]

[Example 3] The powder obtained in the example 3 of powder production was classified by the air-current classification by 7 micrometers. The mean particle diameter of powder 7 micrometers or less was 4 micrometers. An organic titanium compound (isopropyl JIMETAAKURIRU isostearyl titanate) is 3 ten to 2 g/cm in 100g of classification powder. It distributed in the toluene solution and stirred for 2 hours. Then, solid liquid separation was filtered and carried out. The amount of titanium components of processing powder was measured by ICP. The amount of titanium components was 120 ppm of electric conduction powder. It is PbO-B2 O3-SiO2 to the processing powder 100 weight section. Glass frit 1 weight section (490 degrees C of softening temperatures), The 0.01 weight section, the ethyl cellulose 0.2 weight section, the butyral resin 1 weight section, the cuprous-oxide powder 1 weight section, the lead oxide powder 0.1 weight section, the zinc-oxide powder 0.02 weight section, and the oxidation way ****** 0.1 weight section were added, and the PbO-B2 O3-ZnO glass frit (410 degrees C of softening temperatures) (amount of titanium components of 1 ppm) 6 weight section and the organic titanium compound (isopropyl TORIISO stearyl titanate) which were processed with the same organic titanium compound as copper alloy powder were considered as the paste. When the titanium component in the solution of a paste was filtered and a part for a solution was measured, they were the 0.008 weight sections to the electric conduction powder 100 weight section.

[0033] The viscosity of a paste was 200 Pa-s. The viscosity after one-month neglect is 210 Pa-s, and there was almost no viscosity change. Moreover, there was also no sedimentation of a particle. The obtained paste is printed on an alumina substrate and it is 850 degrees C. It calcinated in nitrogen-gas-atmosphere mind for 10 minutes. DOPU to 500 degrees C at this time 50 ppm of oxygen. baking -- the resistance of a conductor was as good as 2.3mohm/**. Moreover, migration-proof was as good as 340 seconds. In early stages, it is high and bond strength is [3kg and] 150 degrees C. It was as high as 2.3kg also after 1000-hour neglect. Solder wettability is 230 degrees C. It was good also after 2-hour neglect.

[0034]

[Comparative Example(s)]

[0035]

[The example 1 of a comparison] 5 micrometers or less of the copper alloy powder obtained in the example 4 of powder production were classified with the air-current classifier. The mean particle diameter of the obtained copper alloy powder was 3 micrometers. Furthermore, an organic titanium compound (isopropanal RIRUISOSUTEARIRUJI acrylic titanate) is 3 0.1g/cm in 100g of obtained copper alloy powder. It stirred in the toluene solution and was left for 2 hours. Then, it filtered, copper alloy powder was taken out and the part was measured by ICP. The titanium component was 30 ppm. The PbO-B2 O3-ZnO glass frit (420 degrees C of softening temperatures) (amount of titanium components of 20 ppm) 3 weight section processed with the same organic titanium compound, the ethyl cellulose 0.3 weight section, the butyl carbitol acetate 3 weight section, the dibutyl phthalate 0.5 weight section, and the cuprous-oxide powder 1 weight section were mixed to the obtained copper alloy processing powder 100 weight section, and it considered as the paste. The viscosity of a paste was as good as 200 Pa-s. It was changeless also after one-month neglect at 210 Pa-s and ******. The obtained paste was screen-stenciled on the alumina substrate.

[0036] 900 degrees C It calcinated in nitrogen-gas-atmosphere mind for 10 minutes. The resistance of the electric conduction film was as good as 3mohm/**. 50 seconds and migration-proof nature were bad as a result of the migration-proof trial.

[0037]

[The example 2 of a comparison] 5 micrometers or less were classified with the air-current classifier in the copper powder obtained in the example 5 of powder production. It is the obtained classification powder Organic titanium compound (isopropyl TORIKUMIRU phenyl titanate) 10-3 g/cm3 It processed stirring in a toluene solution for 3 hours, and solid liquid separation was carried out by filtration after that. The titanium component was 20 ppm when some obtained copper processing powder was measured by ICP.

[0038] It is PbO-B2 O3-SiO2 to the obtained copper processing powder 100 weight section. Copper powder 0.5 weight section mixing was carried out the glass frit (460 degrees C of softening temperatures) 3 weight section, the ethyl cellulose 0.2 weight section, the acrylic resin 1 weight section, the butyl-cellosolve 2 weight section, and for a start [oxidation], and it considered as the paste. When the viscosity of a paste was measured, it was 200 Pa-s. After one-month neglect, when measured, it was high with 300 Pa-s.

[0039] A paste is printed on an alumina substrate and it is 850 degrees C. It calcinated in nitrogen-gas-atmosphere mind for 10 minutes. At this time, it doped 200 ppm of oxygen to 500 degrees C. The conductivity of the obtained electric conduction film was as bad as 10mohm/**. Soldering nature was also bad. an example 2 -- the same -- it printed as an outer conductor of a low-temperature baking multilayered circuit board, and calcinated on the same conditions as an example 2. Resistance was as bad as 12mohm/**.

[0040] an example 2 -- the same -- it applied as an outer conductor of a stacked type ceramic condenser, and calcinated on the same conditions. As for capacity, only 1.5% of value of a value of standard was acquired.

[0041]

[The example 3 of a comparison] The powder (surface silver concentration is lower than the average) obtained in the example 6 of powder production was classified by 5 micrometers or less. The mean particle diameter of the obtained powder was 2 micrometers. 100g of classification powder is taken out and it is 10-3 g/cm3 of an organic titanium compound (isopropyl TORIISO stearyl titanate). It processed stirring in a toluene solution for 3 hours. It was 30 ppm when copper alloy processing powder was measured by ICP. the PbO-B2 O3-ZnO glass frit (470 degrees C of softening temperatures) (amount of titanium components of 3 ppm) 2 weight section processed with the same organic titanium compound as copper alloy powder to the processing powder 100 weight section, and the ethyl cellulose 0.2 weight section -- bisumuth-oxide powder 0.3 weight section addition was carried out, and it considered as the paste. It was 200 Pa-s as a result of measurement of viscosity. The viscosity after one-month neglect was quite high with 1050 Pa-s. A paste is printed on an alumina substrate and it is 900 degrees C. It calcinated in nitrogen-gas-atmosphere mind for 10 minutes. At this time, it doped 200 ppm of oxygen to 500 degrees C. The conductivity of the obtained electric conduction film was as high as 20mohm/**. Soldering nature was also bad.

[0042]

[The example 4 of a comparison] The paste was produced by the same presentation except making into 50 weight sections the amount of the glass frit used in the example 1. The amount of content titanium of copper alloy powder was 10 ppm. Viscosity was 300 Pa-s at the time of production. After one-month neglect, it was mostly stable with 290 Pa-s.

[0043] The screen screen-stencil of the produced paste was carried out on the alumina substrate, and it calcinated for 10 minutes in 600-degree-C nitrogen-gas-atmosphere mind. Glass had come floating on the obtained electric conduction film, and resistance was as high as 40mohm/**. Soldering nature was also bad.

[0044]

[The example 5 of a comparison] The paste was adjusted by the same presentation except [all] making into the 0.01 weight section the amount of the glass frit used in the example 1. The amount of titanium components of copper alloy powder was 1 ppm. Viscosity is 150 Pa-s and it was almost changeless with 155 Pa-s after one-month neglect. The obtained paste was screen-stenciled on the mullite substrate, and was calcinated for 10 minutes in 750-degree-C nitrogen-gas-atmosphere mind. Although the conductivity of the obtained conductor is as good as 2mohm/**, the electric conduction film has peeled.

[0045]

[The example 6 of a comparison] It is the copper alloy powder used in the example 1 10-4 g/cm3 of the same organic titanium compound (isopropyl TORIISOSUTE aisle titanate) as an example 1 It processed in the solution for 2 hours. It was 1300 ppm, when it filtered and the titanium component of copper alloy powder was measured. The PbO-B2 O3-ZnO glass frit (1200 ppm of titanium components) 2 weight section processed with the same organic titanium compound, the acrylic resin 2 weight section, the ethyl cellulose 0.1 weight section, and the cadmium oxide powder (amount of titanium components of 1100 ppm) 0.3 weight section processed with the same organic titanium compound were mixed to the obtained copper alloy powder 100 weight section, and it considered as the paste.

[0046] What was 200 Pa-s at the time of production was thickening with 600Pa and s after one-month neglect as a result of measurement of viscosity. Moreover, the obtained paste was screen-stenciled on the alumina substrate, and was calcinated for 10 minutes in 780-degree-C nitrogen-gas-atmosphere mind. Conductivity was 4.5mohm/**. However, the titanic-acid ghost deposited on the electric conduction film front face, and soldering nature was bad.

[0047]

[The example 7 of a comparison] It is PbO-B2 O3-SiO2 to the copper alloy powder (with no organic titanium processing) 100 weight section used in the example 1 of powder production. The glass frit 2 weight section, the ethyl cellulose 0.5 weight section, and the cuprous-oxide powder 1 weight section were mixed, and it considered as the paste. It is the viscosity of the obtained paste at the production time, there is, and the viscosity after one-month neglect was falling to 20 Pa-s and one half. [of only 50 Pa-s] At this time, sedimentation of the copper alloy powder under paste was seen. Although screen-stenciled, sagging arose and it was not able to print well.

[0048]

[Table 1]

粉末作製例	平均		溶解温度℃	ｱﾄﾏｲｽﾞｶﾞｽ	粒子径μm	表面	
	Ag	Cu				Ag	Cu
1	0.1	0.9	1700	窒素50kg/cm2	11	0.8	0.2
2	0.3	0.7	1700	ﾍﾘｳﾑ30kg/cm2	10	0.9	0.1
3	0.05	0.95	1750	窒素70kg/cm2	9	0.6	0.4
4	0.7	0.3	1700	窒素30kg/cm2	14	0.9	0.1
5	0	1.0	1700	窒素60kg/cm2	10	0	1.0
6	0.05	0.95	1700	空気40kg/cm2	15	0.01	0.99

[0049]

[Effect of the Invention] Even if silver is possible enough on the front face which has a titanium component and carries out the mothball of this invention not only to excelling in oxidation resistance but to a fine line circuit about the paste for baking using the copper alloy powder condensed at high concentration on it, it offers the outstanding paste which has stable viscosity.

[Translation done.]